Experimental report

18/03/2017

Proposal: 6-06-470 **Council:** 4/2016

Title: Understanding the role of Li localstructure in garnet-structured Li7La3Zr2O12 solid electrolytes

Research area: Materials

This proposal is a new proposal

Main proposer: Anna LLORDES

Experimental team: Anna LLORDES
Alejandro FERNANDEZ MARTINEZ

Local contacts: Gabriel Julio CUELLO

Samples: Li6.55Ga0.15La3Zr2O12
Li6.55+yGa0.15La3Zr1-yScyO12

Instrument	Requested days	Allocated days	From	To
D4	4	5	30/08/2016	05/09/2016

Abstract:

Li-stuffed garnet oxides are promising solid electrolyte materials for application in solid-state Li-ion batteries. Our research team is working on the development and understanding of high-performing solid electrolytes based on doped Li7La3Zr2O12 (LLZO). By heterovalent substitutional doping, Li vacancies can be created in the garnet structure, providing fast lithium conduction paths of contiguous tetrahedral and interstitial octahedral sites with disordered Li occupancies. Given the high influence of local structure on the Li+ conductivity, this proposal aims to understand the effect of various cationic substitutions on the disordered Li sublattice.

ILL Experimental report

Title: **Understanding the role of Li local structure in garnet-structured $Li_7La_3Zr_2O_{12}$ solid electrolytes**	*Experiment number* **6-06-470**

Experimental team

Anna Llordes, CIC ENERGIGUNE, Alava, Spain

Alejandro Fernandez-Martinez, ISTerre, CNRS & Univ. Grenoble Alpes

Dates: **30/08/2016 to 05/09/2016**

Local contacts: **Gabriel J. Cuello**

1. *Goal of the experiment*

Li-stuffed garnet oxides are promising solid electrolyte materials for application in solid-state Li-ion batteries. Our research team is working on the development and understanding of high-performing solid electrolytes based on doped $Li_7La_3Zr_2O_{12}$ (LLZO). By heterovalent substitutional doping, Li vacancies can be created in the garnet structure, providing fast lithium conduction paths of contiguous tetrahedral and interstitial octahedral sites with disordered Li occupancies. Given the high influence of local structure on the Li^+ conductivity, this proposal aims to understand the effect of various cationic substitutions on the disordered Li sublattice.

Target substitution sites included Zr^{4+} (in octahedral coordination), La^{3+} (in dodecahedral coordination) or Li^+ sites, for which the last approach requires the smallest substituent concentration but blocks Li-Li bridges. We have shown that the latter strategy, counter-intuitively, is the best for maximizing conductivity. In particular, we have developed a family of fast Li-conducting garnets $Li_{7-3x}Ga_xLa_3Zr_2O_{12}$ ($0 \le x \le 0.3$), synthesized by citrate-nitrate method and using an atmosphere-controlled protocol.

2. *Results*

The following samples, with the general formula $Li_{7-3x+y}Ga_{0.15}La_3Zr_{2-y}Sc_yO_{12}$, were meaured at D4:

1) **Ga_a:** $Li_{6.55}Ga_{0.15}La_3Zr_2O_{12}$ (x=0.15; y=0)
2) **Ga_b**: $Li_{6.55}Ga_{0.15}La_3Zr_2O_{12}$ (x=0.15; y=0, *replicate)*
3) **Ga_Sc_0p1a**: $Li_{6.65}Ga_{0.15}La_3Zr_{1.90}Sc_{0.10}O_{12}$ (x=0.15; y=0.10*)*
4) **Ga_Sc_0p1b**: $Li_{6.65}Ga_{0.15}La_3Zr_{1.90}Sc_{0.10}O_{12}$ (x=0.15; y=0.10, *replicate)*
5) **Ga_Sc_0p15b**: $Li_{6.70}Ga_{0.15}La_3Zr_{1.85}Sc_{0.15}O_{12}$ (x=0.15; y=0.15*)*
6) **LLZO_Tg**: $Li_7La_3Zr_2O_{12}$ (x=0; y=0)

These samples represent different compositions of interest to investigate the interplay between metal substitution, Li local structure and Li-ion conductivity in ceramic electrolytes. Elucidating the Li^+ local environment is of great importance to fundamentally understand its role on the Li-ion dynamics properties of doped $Li_7La_3Zr_2O_{12}$ (LLZO) garnet systems. To do so, the Neutron Total Scattering measurements acquired in D4 and Pair

Distribution Function (PDF) analyses will be further combined with Reverse Monte Carlo and Electrochemical Impedance Spectroscopy analyses.

Background, multiple-scattering, absorption and inelasticity corrections were performed using *CORRECT*. The corrected patterns are shown in Figure 1.

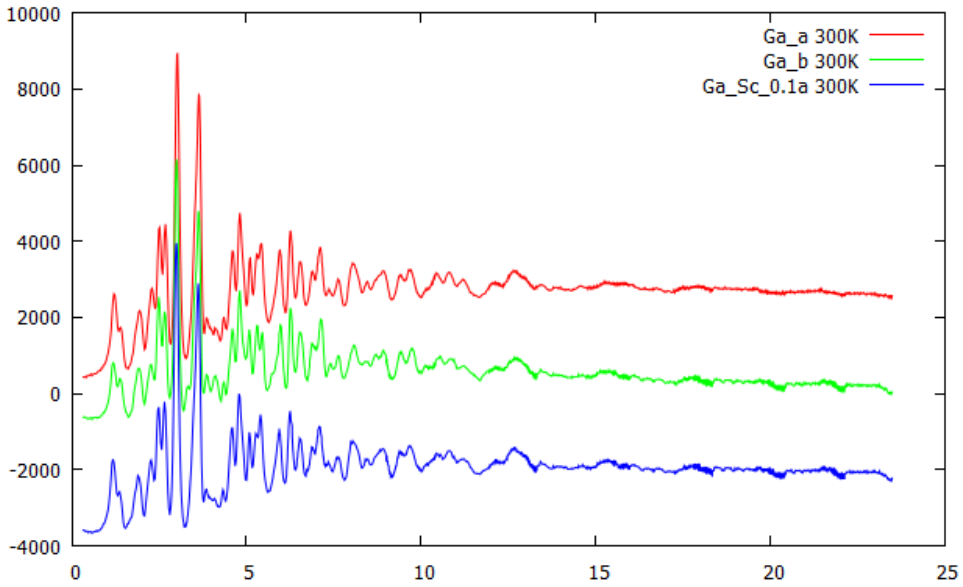

Figure 1. Some representative corrected diffraction patterns (x axis is Q in $Å^{-1}$; y axis is counts in arbitrary units) of the different samples studied. Some noise at high Q needs to be further corrected.

3. Perspectives

A new D4 proposal has been submitted and accepted (experiment not yet performed, planned for the end of 2017) to study the same type of samples but enriched in ^{7}Li. Those data will be combined with the present dataset to obtain partial pair distribution functions involving only Li atoms. These pPDFs will be compared to results from DFT calculations, with the aim of obtaining atomic-level information of the conduction mechanisms in these solid electrolytes.